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3	Full name, address and postcode of the or of each applicant (underline all surnames)	JOHNSON MATTHEY LTD 2-4 Cockspur Street Trafalgar Square London SW1Y 5BQ		
	Patents ADP Number (if you know it)	8519803001 EA		
	If the applicant is a corporate body, give the country/state of its incorporation	United Kingdom		
4	Title of the invention	CATALYST FOR MANUFACTURE OF ESTERS		
5	Name of Your Agent (if you have one)	GIBSON, Sara Hillary Margaret		
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Patents Form 1/77

Catalyst for manufacture of esters

The present invention relates to a catalyst composition which is particularly useful in the manufacture of esters, especially polyesters, and to manufacturing processes using the catalyst composition and also to ester products containing residues of the catalyst  
5 composition.

Certain metals and metal-containing compositions are well known for use to catalyse ester-forming reactions, including esterification and transesterification. Titanium compounds such as titanium alkoxides may be used in the manufacture of polyesters in addition to or in place  
10 of other metal compounds such as antimony compounds. Antimony compounds are very commonly used catalysts for polyester manufacture but have certain disadvantages, which include the inherent toxicity of antimony and also the fact that antimony residues may remain in the polyester, giving a grey colour or, in extreme cases, small visible particles in the polyester. Therefore titanium catalysts, which are highly active esterification catalysts,  
15 provide attractive alternatives to antimony in polyester manufacture in order to reduce or eliminate the requirement for antimony compounds. Titanium catalysts, however, have the disadvantage that the titanium compounds remaining in the polymer tend to produce a yellow colouration. If the final use of the polyester product requires a neutral-coloured or "water-white" material, the colour of the polyester may be adjusted by adding blue-ing  
20 compounds or toners. Inorganic toners such as cobalt acetate are common although a desire to reduce the cobalt content of the polyester has prompted an increase in the use of organic dyes to counteract the yellow colour imparted by titanium catalysts. The need for colour-management of the polyester by the addition of dyes or toners is inconvenient and adds to the costs of polyester production therefore it is desirable to reduce or avoid the need  
25 to use toners or other colour management additives.

It is therefore an object of the invention to provide an improved catalyst composition for use in the production of esters. It is a further object of the invention to provide a catalyst composition which may be used in the production of polyesters and which produces a  
30 polyester of reduced yellow colouration compared with known titanium-based catalyst compositions.

In EP-A-0812818, a process for the preparation of an ester comprises carrying out an esterification in the presence of a catalyst comprising the reaction product of an orthoester or  
35 a condensed orthoester of titanium or zirconium, an alcohol containing at least two hydroxyl groups, a 2-hydroxy acid and a base. These catalysts are more stable than simple titanium alkoxide catalysts and are useful in producing polyester of better colour. There is, however, no suggestion that selection of certain compounds as bases may produce an improved catalyst of the present invention.

- WO01/56694 discloses a catalyst composition suitable for use as a catalyst for the preparation of an ester, including a polyester, comprising an organometallic compound which is a complex of first metal selected from the group consisting of titanium and zirconium, a
- 5 second metal selected from the group consisting of germanium, antimony and tin and a carboxylic acid, preferably in the presence of an alcohol having at least two hydroxy groups and a base. Although these bi-metallic complexes contain a base, there is no disclosure that selection of TEAH as a base would lead to any particular advantage over the preferred inorganic bases.
- 10 WO02/42537 discloses that a combination of a catalyst of the type disclosed in EP-A-0812818 with a second catalyst component selected from a compound of antimony, germanium or tin, is particularly effective in the manufacture of polyester for fibre spinning applications. Although quaternary ammonium compounds, including tetrabutyl ammonium
- 15 hydroxide, tetraethylammonium hydroxide, are mentioned as suitable bases, there is no disclosure that the catalyst compositions of the present invention are particularly effective in producing a polyester having reduced yellowness in the absence of a second metal compound.
- 20 According to the invention, we provide a catalyst suitable for use in an esterification reaction comprising the reaction product of
- a compound of titanium, zirconium or hafnium
  - an alcohol containing at least two hydroxyl groups,
  - a 2-hydroxy carboxylic acid and
  - 25 d) a quaternary ammonium compound selected from the group consisting of tetraethylammonium hydroxide and tetramethylammonium hydroxide.

The compound of titanium, zirconium or hafnium is preferably an alkoxide or condensed alkoxide. Such alkoxides have the formula  $M(OR)_4$  in which M is titanium, zirconium or

30 hafnium and R is an alkyl group. More preferably R contains 1 to 6 carbon atoms and particularly suitable alkoxides include tetraisopropoxy titanium, tetra-n-butoxy titanium, tetra-n-propoxy zirconium and tetra-n-butoxy zirconium.

The condensed alkoxides suitable for preparing the catalysts useful in this invention are typically prepared by careful hydrolysis of titanium or zirconium alkoxides and are frequently

35 represented by the formula  $R^1O[M(OR^1)_2O]_nR^1$  in which  $R^1$  represents an alkyl group and M represents titanium or zirconium. Preferably, n is less than 20 and more preferably is less than 10. Preferably  $R^1$  contains 1 to 6 carbon atoms and useful condensed alkoxides

include the compounds known as polybutyl titanate, polyisopropyl titanate and polybutyl zirconate.

Preferably the alcohol containing at least two hydroxyl groups is a dihydric alcohol e.g. 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butane diol or a dihydric alcohol containing  
5 a longer chain such as diethylene glycol or a polyethylene glycol. Particularly preferred is 1,2-ethanediol or 1,4-butane diol. The catalyst can also be prepared from a polyhydric alcohol such as glycerol, trimethylolpropane or pentaerythritol. When the catalyst is intended for polyester manufacture, the alcohol containing at least two hydroxyl groups is preferably of a similar composition to that used in the polyesterification reaction.

10 Preferably the catalyst comprises from 2 to 12 moles of dihydric alcohol to each mole of the titanium, zirconium or hafnium. More preferably the reaction product contains 4 to 8 moles dihydric alcohol per mole of titanium, zirconium or hafnium. The prepared catalyst may be diluted in a further quantity of the dihydric alcohol.

Preferred 2-hydroxy carboxylic acids include lactic acid, citric acid, malic acid and tartaric  
15 acid. Some suitable acids are supplied as hydrates or as aqueous mixtures. Acids in this form as well as anhydrous acids are suitable for preparing the catalysts used in this invention. The preferred molar ratio of acid to titanium or zirconium in the reaction product is 1 to 4 moles per mole of titanium or zirconium. More preferably the catalyst contains 1.5 to 3.5 moles of 2-hydroxy acid per mole of titanium or zirconium.

20 The molar ratio of quaternary ammonium compound to 2-hydroxy carboxylic acid is in the range 0.05 to 0.79 : 1. In the case of citric acid (a tribasic acid), the preferred amount is in the range 0.01 to 0.6 moles quaternary ammonium compound per mole of 2-hydroxy acid. In general, the amount of quaternary ammonium compound present is usually in the range 0.05 to 4 moles per mole of titanium or zirconium and preferably the amount of quaternary  
25 ammonium compound is from 2 to 3 moles per mole of titanium or zirconium

It is frequently convenient to add water together with the quaternary ammonium compound when preparing the catalysts.

The catalyst can be prepared by mixing the components (alkoxide or condensed alkoxide, dihydric alcohol, 2-hydroxy acid and quaternary ammonium compound) with removal of any  
30 by-product, (e.g. isopropyl alcohol when the alkoxide is tetraisopropoxytitanium), at any appropriate stage. In one preferred method the alkoxide or condensed alkoxide and dihydric alcohol are mixed and subsequently, 2-hydroxy acid and then quaternary ammonium compound are added or a pre-neutralised 2-hydroxy acid solution, is added. In an alternative preferred method the alkoxide or condensed alkoxide is reacted with the 2-  
35 hydroxy acid and by-product alcohol is removed. Quaternary ammonium compound is then

added to this reaction product followed by dilution with a dihydric alcohol to produce the reaction product which is a catalyst of the invention. If desired, further by-product alcohol can then be removed by distillation. The catalyst may be diluted in a solvent, which is preferably the alcohol to be used in the esterification reaction. For example, if the catalyst is  
5 to be used for making polyethylene terephthalate, then the catalyst may be diluted in 1,2-ethanediol.

The esterification reaction of the process of the invention can be any reaction by which an ester is produced. The reaction may be a direct esterification in which a carboxylic acid or its anhydride react with an alcohol to form an ester; or a transesterification (alcoholysis) in  
10 which a first alcohol reacts with a first ester to produce an ester of the first alcohol and a second alcohol produced by cleavage of the first ester; or a interesterification reaction in which two esters are reacted to form two different esters by exchange of alkoxy radicals.

Many carboxylic acids and anhydrides can be used in direct esterification including saturated and unsaturated monocarboxylic acids such as stearic acid, isostearic acid, capric acid,  
15 caproic acid, palmitic acid, oleic acid, palmitoleic acid, triacontanoic acid, benzoic acid, methyl benzoic acid and salicylic acid, dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, sebacic acid, adipic acid, azelaic acid, succinic acid, fumaric acid, maleic acid, naphthalene dicarboxylic acid and pamoic acid and anhydrides of these acids and polycarboxylic acids such as trimellitic acid, citric acid, trimesic acid, pyromellitic acid  
20 and anhydrides of these acids. Alcohols frequently used for direct esterification include aliphatic straight chain and branched monohydric alcohols such as butyl, pentyl, hexyl, octyl and stearyl alcohols and polyhydric alcohols such as glycerol and pentaerythritol. A preferred process of the invention comprises reacting 2-ethylhexanol with phthalic anhydride to form bis(2-ethylhexyl)phthalate.

25

The esters employed in an alcoholysis reaction are generally the lower homologues such as methyl, ethyl and propyl esters since, during the esterification reaction, it is usual to eliminate the displaced alcohol by distillation. Such esters of the acids suitable for direct esterification are used in the process of the invention. Frequently (meth)acrylate esters of longer chain  
30 alcohols are produced by alcoholysis of esters such as methyl acrylate, methyl methacrylate, ethyl acrylate and ethyl methacrylate. Typical alcohols used in alcoholysis reactions include butyl, hexyl, n-octyl and 2-ethyl hexyl alcohols and substituted alcohols such as dimethylaminoethanol.

When the esterification reaction is a transesterification between two esters, generally the  
35 esters will be selected so as to produce a volatile product ester which can be removed by distillation.

Polymeric esters can be produced by processes involving direct esterification or transesterification and a particularly preferred embodiment of the process of the invention is a polyesterification reaction in the presence of the catalyst described hereinbefore. In a polyesterification reaction polybasic acids or esters of polybasic acids are usually reacted with polyhydric alcohols to produce a polymeric ester, often via a diester intermediate product. Linear polyesters are produced from dibasic acids such as those mentioned hereinbefore or esters of said dibasic acids and dihydric alcohols. Alternatively, the preparation of polyesters may be achieved starting from an ester (typically a low alkyl ester) of a dicarboxylic acid, which may be e.g. a C<sub>1</sub> – C<sub>6</sub> alkyl ester of any of the di- or poly-carboxylic acids mentioned above. Of these, methyl esters such as, in particular dimethyl terephthalate or dimethyl naphthalate, are preferred starting materials for the preparation of polyesters. Preferred polyesterification reactions according to the invention include the reaction of terephthalic acid or dimethyl terephthalate with 1,2-ethanediol (ethylene glycol) to produce polyethylene terephthalate (PET), with 1,3-propane diol to form polypropylene terephthalate (also known as poly(trimethylene)terephthalate or PTT), or with 1,4-butanediol (butylene glycol) to produce polybutylene terephthalate (PBT) or reaction of naphthalene dicarboxylic acid with 1,2-ethanediol to produce polyethylene naphthalate (PEN). Other glycols such as 1,6-hexanediol, and pentaerythritol are also suitable for preparing polyesters.

The catalyst and process of the present invention are particularly suitable for the preparation of PET, PBT, or PTT by the reaction of terephthalic acid or an ester thereof with 1,2-ethanediol, 1,4-butane diol, or 1,3-propane diol. We have found that the catalyst and process of the invention show numerous benefits compared with the known titanium alkoxide catalysts.

A typical process for the preparation of a polyester such as polyethylene terephthalate comprises two stages. In the first stage dimethyl terephthalate or terephthalic acid is reacted with 1,2-ethanediol to form a prepolymer and the by-product methanol or water is removed. The prepolymer is subsequently heated in a second stage under reduced pressure to remove 1,2-ethanediol and form a long chain polymer. Either or both these stages may comprise a process according to this invention. A typical process for the preparation of polybutylene terephthalate is similar although in the first stage dimethyl terephthalate is normally used and the dihydric alcohol used is 1,4-butanediol. Processes may be operated either on a batch or a continuous basis. A preferred means of adding the catalyst compositions of this invention to a polyesterification reaction is in the form of a solution in the glycol being used (e.g. ethylene glycol in the preparation of polyethylene terephthalate). This method of addition is applicable to addition of the catalyst composition to the polyesterification reaction at the first stage or at the second stage.



The esterification reaction of the invention can be carried out using any appropriate, known technique for an esterification reaction.

In direct esterification the acid or anhydride and an excess of alcohol are typically heated, if necessary in a solvent, in the presence of the catalyst. Water is usually the by-product of the  
5 reaction and this is removed, as an azeotrope with a boiling mixture of solvent and/or alcohol. Generally, the solvent and/or alcohol mixture which is condensed is immiscible with water which is therefore separated before solvent and/or alcohol are returned to the reaction vessel. When reaction is complete the excess alcohol and, when used, solvent are evaporated. In contrast to prior art esterification processes, it is not generally necessary to  
10 remove the catalyst from the reaction mixture. A typical direct esterification reaction is the preparation of bis(2-ethylhexyl) phthalate which is prepared by mixing phthalic anhydride and 2-ethyl hexanol. An initial reaction to form a monoester is fast but the subsequent conversion of the monoester to diester is carried out by refluxing in the presence of the catalyst at a temperature of 180-200°C until all the water has been removed. Subsequently the excess  
15 alcohol is removed.

In an alcoholysis reaction, the ester, first alcohol and catalyst are mixed and, generally, the product alcohol (second alcohol) is removed by distillation often as an azeotrope with the ester. Frequently it is necessary to fractionate the vapour mixture produced from the alcoholysis in order to ensure that the second alcohol is separated effectively without  
20 significant loss of product ester or first alcohol. The conditions under which alcoholysis reactions are carried out depend principally upon the components of the reaction and generally components are heated to the boiling point of the mixture used.

A preferred process of the invention is the preparation of polyethylene terephthalate. A typical batch production of polyethylene terephthalate is carried out by charging terephthalic  
25 acid and ethylene glycol to a reactor along with catalyst composition, if desired, and heating the contents to 260 - 270° C under a pressure of about 0.3 Mpa (40 psi). Reaction commences as the acid dissolves and water is removed. The product is transferred to a second autoclave reactor and catalyst composition is added, if needed. The reactor is heated to 285 - 310° C under an eventual vacuum of 100 Pa (1 mbar) to remove ethylene  
30 glycol by-product. The molten product ester is discharged from the reactor, cooled and chipped. The chipped polyester may be then subjected to solid state polymerisation, if appropriate.

A second preferred process of the invention is the preparation of polybutylene terephthalate.  
35 A typical batch production of polybutylene terephthalate is carried out by charging terephthalic acid and 1,4 butanediol to a reactor along with catalyst if desired and heating the contents to 170 - 210°C under a pressure of about 0.3 MPa. Reaction commences as the

acid dissolves at about 230°C and water is removed. The product is transferred to a second autoclave reactor and catalyst is added, if needed. The reactor is heated to 240 - 260°C under an eventual vacuum of 100 Pa to remove 1,4 butanediol by-product. The molten product ester is discharged from the reactor, cooled and chipped. Conventional additives to  
5 polyesterification reactions, such as colour modifiers (e.g. cobalt compounds, pigments or dyes), stabilisers (especially those based on phosphorus compounds e.g. phosphoric acid or phosphate ester species), fillers etc may also be added to the polyester reaction mixture.

The amount of catalyst used in the process of the invention generally depends upon the titanium or zirconium content, expressed as Ti or Zr, of the catalyst. Usually the amount is  
10 from 1 to 1000 parts per million (ppm) on weight of product ester for direct or transesterification reactions. Preferably the amount is from 2 to 450 ppm on weight of product ester and more preferably 5 to 50 ppm on weight of product ester. In polyesterification reactions the amount used is generally expressed as a proportion of the weight of product polyester and is usually from 5 to 500 ppm expressed as Ti or Zr based on  
15 product polyester. Preferably the amount is from 5 to 150 ppm expressed as Ti or Zr.

The process of this invention has been shown to effectively produce esters and polyesters at an economical rate.

The invention is illustrated by the following examples.

20 Example 1 (3 moles TEAH)

A 50% w/w aqueous citric acid solution (959 g, 2.5 moles citric acid) was put in a flask. To the stirred solution was slowly added titanium isopropoxide (284g, 1 mole) (VERTEC™ TIPT) and 100 g (1.6 moles) of isopropanol (IPA). This mixture was heated to 90 °C under reflux for 1 hour to yield a hazy solution and then distilled under vacuum to remove free  
25 water and isopropanol (300g). The product was cooled below 50°C and 35 %w/w aqueous tetraethyl ammonium hydroxide (TEAH) (1262 g, 3 moles) was added slowly to the stirred solution followed by 496 g (8 moles) of ethylene glycol and heated under vacuum to remove free water/isopropanol (1178 g). A further quantity of water (34g) and ethylene glycol (631 g) was added to the product which was then refluxed at 90 °C for 60 minutes. The resulting  
30 product catalyst composition contained 2.1% Ti.

Example 2 (2 moles TEAH)

A 50% w/w aqueous citric acid solution (480 g, 1.25 moles citric acid) was put in a flask. To the stirred solution was slowly added titanium isopropoxide (142g, 0.5 mole) and 50 g (0.8  
35 moles) of isopropanol. This mixture was heated to 90 °C under reflux for 1 hour to yield a hazy solution and then distilled under vacuum to remove free water and isopropanol (151g).

The product was cooled below 50°C and 35 %w/w aqueous tetraethyl ammonium hydroxide (421 g, 1 mole) was added slowly to the stirred solution followed by 248 g (4 moles) of ethylene glycol and heated under vacuum to remove free water/isopropanol (378 g). A further quantity of water (17g) and ethylene glycol (315 g ) was added to the product which  
5 was then refluxed at 90 °C for 60 minutes. The resulting product catalyst composition contained 2.1% Ti.

#### Example 3 (1 mole TEAH)

A 50% w/w aqueous citric acid solution (480 g, 1.25 moles citric acid) was put in a flask. To  
10 the stirred solution was slowly added titanium isopropoxide (142g, 0.5 mole) and 50 g (0.8 moles) of isopropanol. This mixture was heated to 90 °C under reflux for 1 hour to yield a hazy solution and then distilled under vacuum to remove free water and isopropanol (151g). The product was cooled below 50°C and 35 %w/w aqueous tetraethyl ammonium hydroxide (210 g, 0.5 moles) was added slowly to the stirred solution followed by 248 g (4 moles) of  
15 ethylene glycol and heated under vacuum to remove free water/isopropanol (168 g). A further quantity of water (17g) and ethylene glycol (315 g ) was added to the product which was then refluxed at 90 °C for 60 minutes. The resulting product catalyst composition contained 2.1% Ti.

#### Example 4 (3 mole TMAH)

A 50% w/w aqueous citric acid solution (240 g, 0.62 moles citric acid) was put in a flask. To the stirred solution was slowly added titanium isopropoxide (71g, 0.25 mole) and 25 g (0.42 moles) of isopropanol. This mixture was heated to 90 °C under reflux for 1 hour to yield a hazy solution and then distilled under vacuum to remove free water and isopropanol (74g).  
25 The product was cooled below 50°C and 25 %w/w aqueous tetramethyl ammonium hydroxide (274 g, 0.75 moles) was added slowly to the stirred solution followed by 124 g (2 moles) of ethylene glycol and heated under vacuum to remove free water/isopropanol (253 g). A further quantity of water (9g) and ethylene glycol (158 g ) was added to the product which was then refluxed at 90 °C for 60 minutes. The resulting product catalyst composition  
30 contained 2.1% Ti.

#### Example 5 (2 mole TMAH: mole Ti)

A 50% w/w aqueous citric acid solution (240 g, 0.62 moles citric acid) was put in a flask. To the stirred solution was slowly added titanium isopropoxide (71g, 0.25 mole) and 25 g (0.42  
35 moles) of isopropanol. This mixture was heated to 90 °C under reflux for 1 hour to yield a hazy solution and then distilled under vacuum to remove free water and isopropanol (75g). The product was cooled below 50°C and 25 %w/w aqueous tetramethyl ammonium hydroxide (182 g, 0.50 moles) was added slowly to the stirred solution followed by 124 g (2 moles) of ethylene glycol and heated under vacuum to remove free water/isopropanol (161

g). A further quantity of water (9g) and ethylene glycol (158 g ) was added to the product which was then refluxed at 90 °C for 60 minutes. The resulting product catalyst composition contained 2.1% Ti.

#### 5 Example 6 (1 mole TMAH)

A 50% w/w aqueous citric acid solution (240 g, 0.62 moles citric acid) was put in a flask. To the stirred solution was slowly added titanium isopropoxide (71g, 0.25 mole) and 25 g (0.42 moles) of isopropanol. This mixture was heated to 90 °C under reflux for 1 hour to yield a hazy solution and then distilled under vacuum to remove free water and isopropanol (75g).

- 10 The product was cooled below 50°C and 25 %w/w aqueous tetramethyl ammonium hydroxide (91 g, 0.25 moles) was added slowly to the stirred solution followed by 124 g (2 moles) of ethylene glycol and heated under vacuum to remove free water/isopropanol (70g). A further quantity of water (9g) and ethylene glycol (158 g ) was added to the product which was then refluxed at 90 °C for 60 minutes. The resulting product catalyst composition
- 15 contained 2.1% Ti.

#### Example 7 (comparative) (3 moles Choline)

- A 50% w/w aqueous citric acid solution (480 g, 1.25 moles citric acid) was put in a flask. To the stirred solution was slowly added titanium isopropoxide (142g, 0.5 mole) and 10 g (0.16
- 20 moles) of isopropanol . This mixture was heated to 90 °C under reflux for 1 hour to yield a hazy solution and then distilled under vacuum to remove free water and isopropanol (112g). The product was cooled below 50°C and 45 %w/w aqueous choline hydroxide (403 g, 1.5 moles) was added slowly to the stirred solution followed by 284 g (4.5 moles) of ethylene glycol and heated under vacuum to remove free water/isopropanol (342 g). A further
- 25 quantity of water (27g) and ethylene glycol (286 g ) was added to the product which was then refluxed at 90 °C for 60 minutes. The resulting product catalyst composition contained 2.1% Ti.

#### Example 8 (3 mole NH<sub>4</sub>OH)

- 30 A 50% w/w aqueous citric acid solution (480 g, 1.25 moles citric acid) was put in a flask. To the stirred solution was slowly added titanium isopropoxide (142g, 0.50 mole) and 10 g (0.17 moles) of isopropanol. This mixture was heated to 90 °C under reflux for 1 hour to yield a hazy solution and then distilled under vacuum to remove free water and isopropanol (112g). The product was cooled below 50°C and 28 %w/w aqueous ammonium hydroxide (188 g,
- 35 0.50 moles) was added slowly to the stirred solution followed by 248 g (4 moles) of ethylene glycol and heated under vacuum to remove free water/isopropanol 363g. A further quantity of water (46g) and ethylene glycol (503 g ) was added to the product which was then refluxed at 90 °C for 60 minutes. The resulting product catalyst composition contained 2.1% Ti.

**EXAMPLE 9 (COMPARATIVE)**

- The procedure of Example 1 was followed but using 132.5 g, (0.63 moles) of citric acid, 72.0 g, (0.25 moles) of titanium isopropoxide, 94.9 g, (0.76 moles) of 32 %w/w aqueous sodium hydroxide and 125.5 g, (2.0 moles) of ethylene glycol. The product was a slightly hazy, very pale yellow liquid (Ti content 3.85 % by weight).

**EXAMPLE 10 (COMPARATIVE)**

- The procedure of Example 1 was followed but using 132.5 g, (0.63 moles) of citric acid, 72.0 g, (0.25 moles) of titanium isopropoxide, 31 g, (0.25 moles) of 32 %w/w aqueous sodium hydroxide and 125.5 g, (2.0 moles) of ethylene glycol. The product was a slightly hazy, very pale yellow liquid (Ti content 3.85 % by weight).

**EXAMPLE 11 Preparation of Poly(ethylene terephthalate) (PET)**

- Ethylene glycol (2.04 kg), isophthalic acid (125g) and terephthalic acid (4.42 kg) were charged to a stirred, jacketed reactor. The catalyst was added and the reactor heated to 226 - 252 °C at a pressure of 40 psi to initiate the first stage direct esterification (DE) process. Water was removed as it was formed with recirculation of the ethylene glycol. On completion of the DE reaction the contents of the reactor were allowed to reach atmospheric pressure before a vacuum was steadily applied. The mixture was heated to 290 ± 2 °C. under vacuum to remove ethylene glycol and yield polyethylene terephthalate. The final polyester was discharged once a constant torque had been reached which indicated an IV of about 0.62. The catalysts were added to produce a Ti content of 8ppm in the polyester reaction mixture. The time for polycondensation (PC) and the intrinsic viscosity (IV) and colour values of the resulting polyesters are shown in Table 1.
- No inorganic or organic toners were added to the polymer. The colour of the polymer was measured using a Byk-Gardner Colourview spectrophotometer. A common model to use for colour expression is the Cielab L\*, a\* and b\* scale where the b\*-value describes yellowness.
- The yellowness of the polymer increases with b\*-value.
- The intrinsic viscosity (IV) was measured by solution viscosity on an 8% solution of the polyester in o-chlorophenol at 25°C.

**Table 1**

Catalyst	IV	PC mins	5 minutes			15 minutes		
			L*	a*	b*	L*	a*	b*
Example 1	0.62	90	74.11	-1.55	6.83	72.83	-1.93	8.70
Example 4	0.62	71	74.44	-2.79	10.43	75.07	-2.04	10.23
Sb <sub>2</sub> O <sub>3</sub> (Comp) (270 ppm)	0.6	122	59.58	-0.83	2.69	61.25	-0.94	3.64
Example 9 (comp) (Av of 5 runs)	0.62	108	70.10	-2.48	14.55	72.55	-2.40	17.16

The results show that the catalysts of the invention give a very rapid polycondensation whilst the product polyester is significantly less yellow than the comparison titanium catalyst of Example 9. The melt stability, as evidenced by the colour change between polymer exiting the reactor after 5 and 15 minutes, is also very good using the catalysts of the invention.

- 5 Compared with the antimony catalyst added at a relatively high concentration, the polycondensation time is much shorter using the catalysts of the invention and the resulting polymer is brighter (higher L\* value) giving the polymer a desirable "sparkle".

#### Example 12 Hydrolysis Test

- 10 The hydrolytic stability of the titanium catalysts was determined by the following method. The required amount of the catalyst containing 350 ppm of Ti was added to 40g of monoethylene glycol and 0.6g of water (1.5%). The solution was thoroughly mixed and placed in a pressurized glass tube which was heated in an oven at 280 °C for 2 hours after which time the tube was removed and allowed to cool to room temperature. Any colour
- 15 change or visible precipitation was recorded. The catalysts tested and the results are shown in Table 2 below.

Table 2

Catalyst	Precipitate	Colour
Example 1	NO	Clear pale yellow solution
Example 3	YES	Hazy yellow solution
Example 4	NO	Clear pale yellow solution
Example 5	YES	Hazy Yellow solution
Example 7	YES	Hazy Yellow solution
Example 8	YES	Hazy dark brown solution
Example 9	NO	Clear yellow solution

## Claims

1. A catalyst suitable for use in an esterification reaction comprising the reaction product of
  - a) a compound of titanium, zirconium or hafnium
  - b) an alcohol containing at least two hydroxyl groups,
  - c) a 2-hydroxy carboxylic acid and
  - d) a quaternary ammonium compound selected from the group consisting of tetraethylammonium hydroxide and tetramethylammonium hydroxide.
  
2. A process for the production of a polyester comprising:
  - a) reacting together a polyhydroxy alcohol with at least one multifunctional carboxylic acid or an ester thereof to form a bis hydroxy ester of the multifunctional carboxylic acid ,
  - b) polycondensing said bishydroxy ester to form a polyester,characterised in that at least one of steps a) and b) is carried out in the presence of a catalyst as claimed in claim 1.

**Abstract**

A catalyst suitable for use in an esterification reaction comprising the reaction product of a compound of titanium, zirconium or hafnium, an alcohol containing at least two hydroxyl groups, a 2-hydroxy carboxylic acid and a quaternary ammonium compound selected from the group consisting of tetraethylammonium hydroxide and tetramethylammonium hydroxide.



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